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Supersymmetry identifies molecular Stark states whose eigenproperties can be obtained analytically

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Supersymmetry identifies molecular Stark states whose eigenproperties can be obtained analytically

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Abstract. We made use of supersymmetric (SUSY) quantum mechanics to find the condition under which the Stark effect problem for a polar and polarizable closed-shell diatomic molecule subjected to collinear electrostatic and nonresonant radiative fields becomes exactly solvable. The condition $\Delta\omega = \frac{\omega^2}{4(m+1)^2}$ connects values of the dimensionless parameters ω and $\Delta\omega$ that characterize the strengths of the permanent and induced dipole interactions of the molecule with the respective fields. The exact solutions are obtained for the $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ family of ‘stretched’ states. The field-free and strong-field limits of the combined-fields problem were found to exhibit supersymmetry and shape invariance, which is indeed the reason why they are analytically solvable. By making use of the analytic form of the $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ wavefunctions, we obtained simple formulae for the expectation values of the space-fixed electric dipole moment, the alignment cosine and the angular momentum squared, and derived a ‘sum rule’ that combines the above expectation values into a formula for the eigenenergy. The analytic expressions for the characteristics of the strongly oriented and aligned states provide direct access to the values of the interaction parameters required for creating such states in the laboratory.

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1. Introduction

Whether a problem in quantum mechanics is exactly solvable is closely related to its supersymmetry (SUSY) [1, 2]. The foundations of supersymmetric quantum mechanics were worked out by Witten in 1981 as an example of SUSY in zero-dimensional field theory [3]. Soon thereafter, supersymmetric quantum mechanics rapidly evolved into a new branch of mathematical physics [1, 2, 4] and reached a peak in 1983—then unnoticed—when Gendenshtein established a connection between SUSY and exact solvability [5]: he demonstrated that Schrödinger’s equation is exactly solvable if the potential and its superpartner exhibit shape invariance. Whereas a supersymmetric Hamiltonian can be constructed for any potential whose ground-state wavefunction is analytic, shape invariance only exists for supersymmetric potentials that are interconvertible by a change of a parameter other than the integration variable itself [6]. Herein, we make use of the methods of supersymmetric quantum mechanics to arrive at exact wavefunctions and other eigenproperties of linear molecules subjected to nonresonant electric fields in closed form.

In our previous work on the molecular Stark effect, we showed that for polar molecules, combined collinear electric and nonresonant radiative fields can synergetically produce spatially oriented pendular states, in which the molecular axis librates over a limited angular range about the common field direction [7]. These directional states comprise coherent superpositions or hybrids of the field-free rotational states $|J, m\rangle$, with a range of J values but a fixed value of m , which remains a good quantum number by virtue of the azimuthal symmetry about the fields. This has proved an effective and versatile means of producing oriented molecules for applications ranging from molecular optics and spectroscopy to chemistry and surface science [8–10]. However, the eigenproperties of the Stark states in question had to be found numerically, typically by diagonalizing a truncated Hamiltonian matrix. Here we show that supersymmetric factorization of the Hamiltonian yields exact wavefunctions $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ in closed form for a particular ratio of the parameters ω and $\Delta\omega$ that determine the interaction strengths of the molecules with the static and radiative fields, respectively.

This paper is organized as follows. In section 2, we first introduce the molecular Stark effect problem for the case of collinear electrostatic and radiative fields. In section 3, we use

methods of supersymmetric quantum mechanics to find solutions to the problem of molecules in combined fields in closed form. We derive a relation between the strengths of the electrostatic and laser fields, ω and $\Delta\omega$, at which the wavefunctions of the $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ states take a simple analytic form and show that SUSY furnishes isospectral partner potentials that can be realized with combined fields. In section 4, we discuss shape invariance of the supersymmetric partner potentials obtained and the general conditions for the exact solvability of the Stark effect problem. In section 5, we investigate the field-free and strong-field limits, where the field strengths ω and $\Delta\omega$ approach, respectively, zero or infinity. We show that in both limits, the problem exhibits SUSY and shape invariance and therefore can be solved exactly. Section 6 gives a summary of the exact closed-form expressions for the properties of molecules in fields obtained from the exact wavefunctions. These properties include the eigenenergy, the space-fixed dipole moment, the alignment cosine and the expectation value of angular momentum. The availability of these otherwise hard-to-come-by properties in closed form allows us to reverse-engineer the problem of finding the interaction parameters required for creating quantum states with preordained characteristics. The main conclusions of this work are summarized in section 7. An appendix surveys the concepts pertinent to exact solvability.

2. Molecules in collinear electric and radiative fields

We consider a $^1\Sigma$ linear molecule with a rotational constant B , a permanent dipole moment μ along the internuclear axis and polarizability components α_{\parallel} and α_{\perp} parallel and perpendicular to the internuclear axis. The molecule is subjected to an electrostatic field $\boldsymbol{\varepsilon}$ combined with a nonresonant laser field of intensity I , whose linear polarization is collinear with $\boldsymbol{\varepsilon}$. With energy expressed in terms of B , the Hamiltonian takes the dimensionless form [11]

$$H = \mathbf{J}^2 + V_{\mu,\alpha}(\theta), \quad (1)$$

with the angular momentum operator

$$\mathbf{J}^2 = -\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) - \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \quad (2)$$

and the interaction potential

$$V_{\mu,\alpha}(\theta) = -\omega \cos\theta - (\Delta\omega \cos^2\theta + \omega_{\perp}). \quad (3)$$

The dimensionless interaction parameters are given as $\omega \equiv \mu\varepsilon/B$ and $\Delta\omega \equiv \omega_{\parallel} - \omega_{\perp}$, with $\omega_{\parallel,\perp} \equiv 2\pi\alpha_{\parallel,\perp}I/(Bc)$.

The common direction of the collinear electrostatic and linearly polarized radiative fields defines an axis of cylindrical symmetry, chosen to be the space-fixed axis Z . The projection, m , of the angular momentum \mathbf{J} on Z is then a good quantum number, while J is not. However, one can use the value of J of the field-free rotational state, $Y_{J,m}(\theta, \phi)$, that adiabatically correlates with the hybrid state as a label, designated by \tilde{J} , so that $\psi_{\tilde{J},m}^{\omega,\Delta\omega}(\theta, \phi) \rightarrow Y_{J,m}(\theta, \phi)$ for $\omega, \Delta\omega \rightarrow 0$. For arbitrary interaction strengths, the solution to the Schrödinger equation with Hamiltonian (1) is an infinite coherent superposition of the field-free wavefunctions

$$|\tilde{J}, m; \omega, \Delta\omega\rangle = \sum_J c_{Jm}^{\tilde{J}}(\omega, \Delta\omega) Y_{Jm}, \quad (4)$$

whose expansion coefficients $c_{j_m}^{\tilde{m}}(\omega, \Delta\omega)$ can be obtained by truncating series (4) at some maximum value of J and then diagonalizing Hamiltonian (1) in the finite basis set of the field-free wavefunctions.

The axial symmetry of the problem allows us to separate angular variables and express the dependence on the azimuthal angle ϕ via the good quantum number m . In this case the Schrödinger equation with Hamiltonian (1) can be recast as

$$\left[-\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) + V_{\mu,\alpha}^{(3D)}(\theta) \right] \psi(\theta) = E\psi(\theta), \quad (5)$$

where the three-dimensional (3D) effective potential is given by

$$V_{\mu,\alpha}^{(3D)}(\theta) = \frac{m^2}{\sin^2\theta} - \omega \cos\theta - \Delta\omega \cos^2\theta. \quad (6)$$

We note that all rotational levels are uniformly shifted by ω_{\perp} . In what follows we use $E = E_{\mu,\alpha} + \omega_{\perp}$ instead of the ‘true’ molecular energy, $E_{\mu,\alpha}$. Moreover, since the Stark effect does not depend on the sign of m , we can define the projection of the angular momentum on Z as a positive quantity, $m \equiv |m|$.

By means of the substitution [12]

$$\psi(\theta) = f(\theta)(\sin\theta)^{-1/2}, \quad (7)$$

the Schrödinger equation (5) can be transformed into a 1D form

$$\left[-\frac{d^2}{d\theta^2} + V_{\mu,\alpha}^{(1D)}(\theta) \right] f(\theta) = 0, \quad (8)$$

where

$$V_{\mu,\alpha}^{(1D)}(\theta) = \frac{m^2 - \frac{1}{4}}{\sin^2\theta} - \omega \cos\theta - \Delta\omega \cos^2\theta - \frac{1}{4} - E \quad (9)$$

is a 1D effective potential, which will be shown to play the role of one of the requisite superpartner potentials leading to ground-state energy $E = E_0$.

3. Supersymmetric factorization of the combined-field Hamiltonian

Here we invoke SUSY to find analytic solutions to equation (8) and subsequently to equation (5). SUSY makes use of the first-order differential operators, $A^{\pm} \equiv \mp \frac{d}{d\theta} + W(\theta)$, with $W(\theta)$ being the superpotential. The superpartner Hamiltonians are defined by

$$H_{\mp} = A^{\pm} A^{\mp} = -\frac{d^2}{d\theta^2} + V_{\mp}^{(1D)}(\theta), \quad (10)$$

with the 1D partner potentials $V_{\pm}^{(1D)}(\theta) \equiv W^2(\theta) \pm W'(\theta)$. The superpartner Hamiltonians have the same energy spectra except for the ground state, and if the eigenfunctions of one of the partner Hamiltonians H_{\mp} are known, the eigenfunctions of the other can be obtained analytically via the intertwining relations [2, 13].

In the case of a molecule in combined fields, we start from the following ansatz for the superpotential:

$$W(\theta) = a \cot(\theta) + q(\theta), \quad (11)$$

where the constant a and the function $q(\theta)$ are to be determined. The first term in equation (11) is the superpotential for a field-free rigid rotor, which is a special case of the Rosen–Morse I potential [2]. The superpotential $W(\theta)$ yields the supersymmetric partner potentials $V_{\pm}^{(1D)}(\theta)$:

$$V_{\pm}^{(1D)}(\theta) \equiv W^2(\theta) \pm W'(\theta) = \frac{a(a \mp 1)}{\sin^2 \theta} + q^2(\theta) \pm q'(\theta) + 2aq(\theta) \cot \theta - a^2. \quad (12)$$

By identifying the effective potential (9) with $V_{-}^{(1D)}(\theta)$ and substituting it into equation (12), we obtain

$$\frac{m^2 - \frac{1}{4}}{\sin^2 \theta} - \omega \cos \theta - \Delta \omega \cos^2 \theta - \frac{1}{4} - E_0 = \frac{a(a+1)}{\sin^2 \theta} + q^2(\theta) - q'(\theta) + 2aq(\theta) \cot \theta - a^2, \quad (13)$$

which is satisfied for

$$q(\theta) = \beta \sin \theta, \quad (14)$$

$$a = -(m + 1/2), \quad (15)$$

$$E_0 = m(m + 1) - \beta^2, \quad (16)$$

and

$$\Delta \omega = \frac{\omega^2}{4(m+1)^2} = \beta^2. \quad (17)$$

Substitution of equations (14) and (15) into equation (11) leads to a superpotential

$$W(\theta) = -\left(m + \frac{1}{2}\right) \cot \theta + \beta \sin \theta, \quad (18)$$

corresponding to the following pair of superpartner potentials:

$$V_{-}^{(1D)}(\theta) = \frac{m^2 - \frac{1}{4}}{\sin^2 \theta} - 2\beta(m+1) \cos \theta - \beta^2 \cos^2 \theta + \beta^2 - m(m+1) - \frac{1}{4}, \quad (19)$$

$$V_{+}^{(1D)}(\theta) = \frac{(m+1)^2 - \frac{1}{4}}{\sin^2 \theta} - 2\beta m \cos \theta - \beta^2 \cos^2 \theta + \beta^2 - m(m+1) - \frac{1}{4}. \quad (20)$$

We note that by identifying the effective potential (9) with $V_{+}^{(1D)}(\theta)$ instead, the result would have been the same for $a = (m - 1/2)$.

Thus, for each value of the good quantum number m , there exists a pair of the supersymmetric partner Hamiltonians H_{-} and H_{+} , which are isospectral and fulfill the following relations:

$$H_{+}(Af_n^{-}(\theta)) = E_n^{-}(Af_n^{-}(\theta)), \quad (21)$$

$$H_{-}(A^{\dagger}f_n^{-}(\theta)) = E_n^{+}(A^{\dagger}f_n^{-}(\theta)), \quad (22)$$

which imply

$$E_n^{+} = E_{n+1}^{-}, \quad E_0^{-} = 0, \quad (23)$$

$$f_n^{+}(\theta) = (E_{n+1}^{-})^{-1/2} Af_{n+1}^{-}(\theta), \quad f_{n+1}^{-}(\theta) = (E_n^{+})^{-1/2} A^{\dagger} f_n^{+}(\theta), \quad (24)$$

$$Af_0^{-}(\theta) = 0. \quad (25)$$

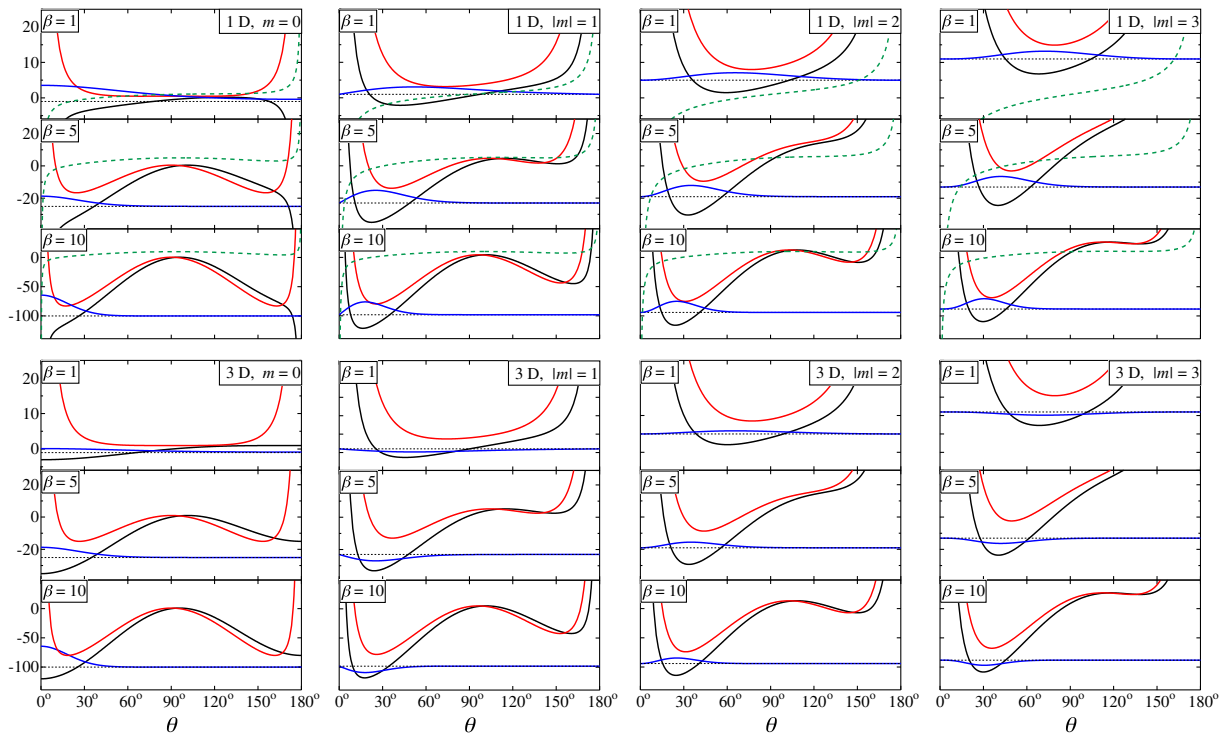


Figure 1. Top panels: 1D supersymmetric partner potentials $V_-^{(1D)}(\theta) + E_0$ (black solid line), $V_+^{(1D)}(\theta) + E_0$ (red solid line), superpotential $W(\theta)$ (green dashed line) and ground-state wavefunction $f_0(\theta)$ (blue solid line) for $|m| = 0, 1, 2$ and 3 and different values of β . Bottom panels: 3D supersymmetric partner potentials, $V_-^{(3D)}(\theta)$ (black solid line) and $V_+^{(3D)}(\theta)$ (red solid line) corresponding to the above 1D potentials, along with the ground-state wavefunction of a molecule in combined fields, $\psi_0(\theta)$ (blue solid line). The eigenenergy of the ground state, $E_0 = m(m+1) - \beta^2$ (in units of B), is shown by the black dotted line.

The ground-state wavefunction $f_0^-(\theta)$ can be obtained from the superpotential (18)

$$f_0^-(\theta) = N \exp\left[-\int_0^\theta W(x) dx\right], \quad (26)$$

which yields the wavefunction in closed form,

$$f_0^-(\theta) = N (\sin \theta)^{(m+1/2)} e^{\beta \cos \theta}. \quad (27)$$

Its normalization constant is given by

$$N = \left[\frac{\Gamma(m + \frac{3}{2})}{2\pi^{3/2} \Gamma(m+1) {}_0F_1(; m + \frac{3}{2}; \beta^2)} \right]^{1/2}, \quad (28)$$

where ${}_0F_1(; a; z)$ is the confluent hypergeometric function [14]. Since the ground-state wavefunction (27) is normalizable and obeys the annihilation condition (25), the SUSY obtained is unbroken [2, 15, 16]. The top panels of figure 1 show the 1D supersymmetric partner potentials $V_\mp^{(1D)}(\theta) + E_0$, the superpotential $W(\theta)$ and the ground-state wavefunction $f_0(\theta)$ for $|m| = 0, 1, 2$ and 3 and different values of the interaction parameter β . As β increases,

the nodeless wavefunction $f_0(\theta)$ becomes strongly confined near the potential minimum. The potentials (19) and (20) come close to each other with growing m and eventually coincide in the limit $m \gg 1$.

By comparing the 1D potentials $V_+^{(1D)}$ and $V_-^{(1D)}$, equations (19) and (20), with equations (5) and (8), we obtain the 3D potentials corresponding to a molecule interacting with the combined fields,

$$V_-^{(3D)}(\theta) = \frac{m^2}{\sin^2 \theta} - 2(m+1)\beta \cos \theta - \beta^2 \cos^2 \theta, \quad (29)$$

$$V_+^{(3D)}(\theta) = \frac{(m+1)^2}{\sin^2 \theta} - 2m\beta \cos \theta - \beta^2 \cos^2 \theta. \quad (30)$$

The ground-state wavefunction of the $V_-^{(3D)}$ potential (corresponding to energy $E_0 = m(m+1) - \beta^2$) then becomes

$$\psi_0(\theta) = N(-1)^m (\sin \theta)^m e^{\beta \cos \theta}. \quad (31)$$

The phase factor $(-1)^m$ leads to the correct asymptotic behavior of the wavefunction, which, for $\beta = 0$, reduces to the ground-state wavefunction of a rigid rotor with $J = m$, $Y_{m,m}(\theta, 0)$.

Equation (30) coincides with the potential for a rigid rotor in the combined fields whose projection quantum number is $m+1$ and whose interaction strengths are related by

$$\Delta\omega = \frac{\omega^2}{4m^2} = \beta^2. \quad (32)$$

Hence we have shown that, given a value of β , the Hamiltonian of a molecule with a projection m of the angular momentum on the combined fields whose interaction parameters are related by equation (17) has the same set of eigenvalues as a molecule with a projection $m+1$ on the combined fields whose interaction parameters are related by equation (32).

The bottom panels of figure 1 show the 3D superpartner potentials, $V_{\mp}^{(3D)}(\theta)$, for a molecule in the combined fields along with the ground-state wavefunctions, $\psi_0(\theta)$, for $|m| = 0, 1$. The permanent dipole term ($\propto \cos \theta$) is asymmetric with respect to $\theta = \pi/2$, whereas the induced-dipole term ($\propto \cos^2 \theta$) is symmetric about $\theta = \pi/2$ and gives rise to a double well for $\alpha_{\parallel} > \alpha_{\perp}$. At large β , $\omega \ll \Delta\omega$ and the coupling between the double well's tunneling doublets results in localizing the ground-state wavefunction in the forward well of either the $V^{(1D)}$ or $V^{(3D)}$ potential, which for $\omega \ll \Delta\omega$ is mainly due to the polarizability interaction. At small β , ω is comparable with $\Delta\omega$ and the effective potential becomes skewed as the forward well becomes deeper at the expense of the backward well. For any $\beta > 0$, the molecule exhibits orientation (as opposed to alignment), which rapidly increases with β .

We note that for $m = 0$ the ground-state level always lies deeper than the potential minima at $\theta = \pi$, since $V(\theta = \pi) - E_0 \equiv 2\beta > 0$. Therefore, for any value of β the molecule remains confined to the potential minimum at $\theta = 0$ and exhibits orientation. For the 'stretched' states of highly rotationally excited molecules, $J = m \gg 1$, the supersymmetric partner potentials (29) and (30) coincide.

4. Shape invariance and exact solvability of the molecular Stark effect problem

Gendenshtein [5] demonstrated that the Schrödinger equation for any of the superpartner potentials, $V_-(\theta, a)$ and $V_+(\theta, a)$, admitting normalizable solutions, is exactly solvable if the

potentials are translationally shape invariant, i.e.

$$V_+(\theta, a_0) + g(a_0) = V_-(\theta, a_1) + g(a_1), \quad (33)$$

where the values a_0 and a_1 of the parameter a pertain to the n th eigenstate with $n = 0$ and $n = 1$, and the function $g(a)$ is independent of θ . The parameter a_1 is a function of a_0 , i.e. $a_1 = p(a_0)$.

If the superpartner potentials satisfy relation (33), the eigenenergies and wavefunctions of H_- can be obtained from [1, 17]

$$E_n^- = g(p^{(n)}(a_0)) - g(a_0), \quad (34)$$

$$f_n^-(\theta, a_0) = A^\dagger(\theta, a_{n-1}) f_0^-(\theta, a_n), \quad (35)$$

where $p^{(n)}(a_0)$ designates the function $p(a)$ applied n times.

Recently, Gangopadhyaya and Mallow demonstrated that condition (33) is equivalent to the following partial differential equation for the superpotential [17, 18]:

$$2W(\theta, a) \left(\frac{\partial W(\theta, a)}{\partial a} \right) - 2 \frac{\partial W(\theta, a)}{\partial \theta} + \frac{\partial g(a)}{\partial a} = 0. \quad (36)$$

Unfortunately, equation (36) is not satisfied for the superpotential $W(\theta, a)$ of equation (18), neither for $a = \beta$ nor for $a = m$, and therefore the partner potentials $V_-^{(1D)}(\theta, a)$ and $V_+^{(1D)}(\theta, a)$ are not shape invariant. Although shape invariance is a sufficient but not necessary condition for exact solvability [19], the Schrödinger equation for a molecule in combined fields is known to be in general unsolvable exactly [11, 14]. We also note that none of the known shape-invariant superpotentials listed, e.g., in [1, 17] leads to exactly solvable partner Hamiltonians that can be experimentally implemented for molecules in nonresonant fields. For reference purposes, we provide a summary of the relationships among exactly solvable, shape invariant and Infeld–Hull factorizable potentials in the [appendix](#).

5. Supersymmetry and shape invariance of the combined-field Hamiltonian in the field-free and strong-field limits

In the field-free limit, $\omega, \Delta\omega \rightarrow 0$, the 3D Schrödinger equation reduces to the one for a rigid rotor:

$$\mathbf{J}^2 \psi(\theta) = E \psi(\theta), \quad (37)$$

whose solutions are spherical harmonics, $\psi(\theta) = Y_{Jm}(\theta, 0)$ pertaining to eigenenergies $E_J = J(J+1)$.

We obtain the expressions for the superpotential and partner potentials of a free rotor by setting $\beta = 0$ in equations (18)–(20):

$$W(\theta) = -\left(m + \frac{1}{2}\right) \cot \theta, \quad (38)$$

$$V_-^{(1D)}(\theta) = \frac{m^2 - \frac{1}{4}}{\sin^2 \theta} - m(m+1) - \frac{1}{4}, \quad (39)$$

and

$$V_+^{(1D)}(\theta) = \frac{(m+1)^2 - \frac{1}{4}}{\sin^2 \theta} - m(m+1) - \frac{1}{4}. \quad (40)$$

This is an obvious result, as for $J = m$ the spectra of two rigid rotors with quantum numbers m and $m + 1$ coincide except for the ground state [12, 20].

Potentials (39) and (40) are seen to be shape invariant, with $a_0 = m$, $a_1 \equiv p(a_0) = a_0 + 1$ and $g(a_n) = a_n(a_n + 1)$, and the superpotential of equation (38) satisfies equation (36). The eigenenergies of the Hamiltonian H_- are obtained from equation (34):

$$E_n^- = n(n + 2m + 1), \quad (41)$$

which for $n = J - m$ coincides with the rigid rotor spectrum, shifted by $-m(m + 1)$. The energy spectrum and wavefunctions of the supersymmetric partner potential V_+ can be obtained via equations (23) and (24).

In the strong-field limit, $\omega, \Delta\omega \rightarrow \infty$, the angular motion of the molecules is confined near $\theta = 0$ and potential (9) can be expanded in powers of θ . On retaining terms up to second order, the potential can be reduced to that of a 3D angular oscillator (librator). The corresponding Schrödinger equation (8) takes the form

$$\left[-\frac{d^2}{d\theta^2} + \frac{\kappa^2\theta^2}{4} + \frac{\ell(\ell+1)}{\theta^2} \right] f(\theta) = \tilde{E} f(\theta), \quad (42)$$

where the eigenenergies are given by

$$\tilde{E}_n \equiv E + \omega + \Delta\omega + \frac{1}{4} = \kappa \left(2n + \ell + \frac{3}{2} \right), \quad n = 0, 1, 2, \dots, \quad (43)$$

and $\kappa^2 = 2(\omega + 2\Delta\omega)$, $\ell = (\pm m - 1/2)$.

The analytic eigenfunctions of the angular harmonic oscillator can be expressed in terms of Laguerre polynomials [2]

$$f_n(\theta) = N\theta^{\ell+1} L_n^{(\ell+1/2)}(x) \exp(-x/2), \quad x \equiv \frac{1}{2}\kappa\theta^2, \quad (44)$$

with

$$N = \left(\frac{\kappa}{2} \right)^{\ell/2+3/4} \left[\frac{2n!}{\Gamma(n+\ell+3/2)} \right]^{1/2} \quad (45)$$

and they vanish at $x \rightarrow 0$ and decay exponentially at $x \rightarrow \infty$.

The corresponding superpotential can be constructed from the ground-state wavefunction, equation (44), with $n = 0$,

$$W(\theta) \equiv -\frac{f_0'(\theta)}{f_0(\theta)} = \frac{\kappa\theta}{2} - \frac{\ell+1}{\theta}, \quad (46)$$

which leads to the supersymmetric partner potentials

$$V_-(\theta) = \frac{\kappa^2\theta^2}{4} + \frac{\ell(\ell+1)}{\theta^2} - \kappa \left(\ell + \frac{3}{2} \right), \quad (47)$$

$$V_+(\theta) = \frac{\kappa^2\theta^2}{4} + \frac{(\ell+1)(\ell+2)}{\theta^2} - \kappa \left(\ell + \frac{1}{2} \right). \quad (48)$$

The potential of equation (47) coincides with the potential of equation (42) shifted by the ground-state energy, $E_0 = -\kappa(\ell + 3/2)$.

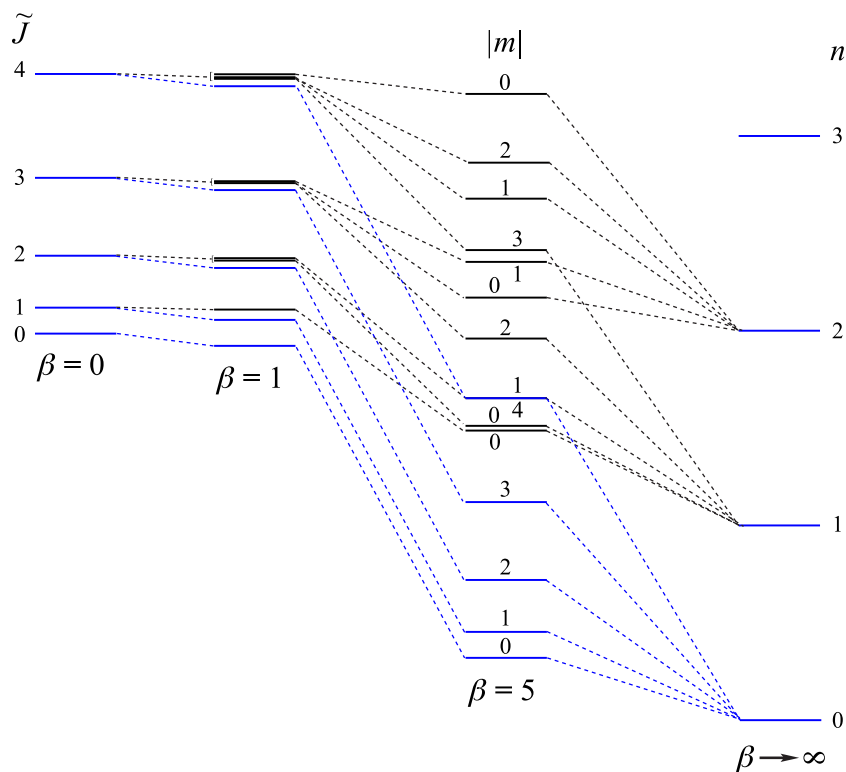


Figure 2. Eigenstates of a molecule in combined fields for different values of β , with exactly solvable cases shown in blue. The equidistant energy levels in the strong-field limit, $\beta \rightarrow \infty$, are labeled by the 3D libration quantum number n and are shown schematically. See text for details.

Potentials (47) and (48) are shape invariant, with the parameters $a_0 = \ell$, $a_1 \equiv p(a_0) = a_0 + 1$ and $g(a_n) = 2\kappa a_n$ and superpotential (46) satisfies equation (36). The eigenenergies of the Hamiltonian H_- can be obtained from equation (34):

$$E_n^- = 2\kappa n, \quad (49)$$

which coincides with the eigenenergies given by equation (43) shifted by $-\kappa\ell - 3/2$. The eigenenergies and eigenfunctions of the superpartner potentials also fulfill equations (23)–(25) and represent a complete analytic solution to the problem.

Figure 2 shows the energy levels of a molecule in combined fields for different values of the field-strength parameter β . In the weak-field limit, $\beta \rightarrow 0$, the energy levels approach those of a free rotor, which is solvable exactly for all the eigenstates. For nonzero but weak fields, $\beta = 1$, the levels become split into $\tilde{J} + 1$ components due to the Stark effect. In this case, the SUSY partner Hamiltonians are not shape invariant, and the problem is analytically solvable only for the ‘stretched states’, corresponding to $\tilde{J} = m$. With increasing interaction strength, the energies of the stretched states come closer to one another and, in the strong-field limit, $\beta \rightarrow \infty$, coalesce into the ground-state level of the 3D harmonic libration. In the strong-field limit, the supersymmetric problem becomes shape-invariant again, and is exactly solvable for all eigenstates in closed form; the equidistant levels are infinitely degenerate and separated by an energy difference of $(2\omega + 4\Delta\omega)^{1/2}$.

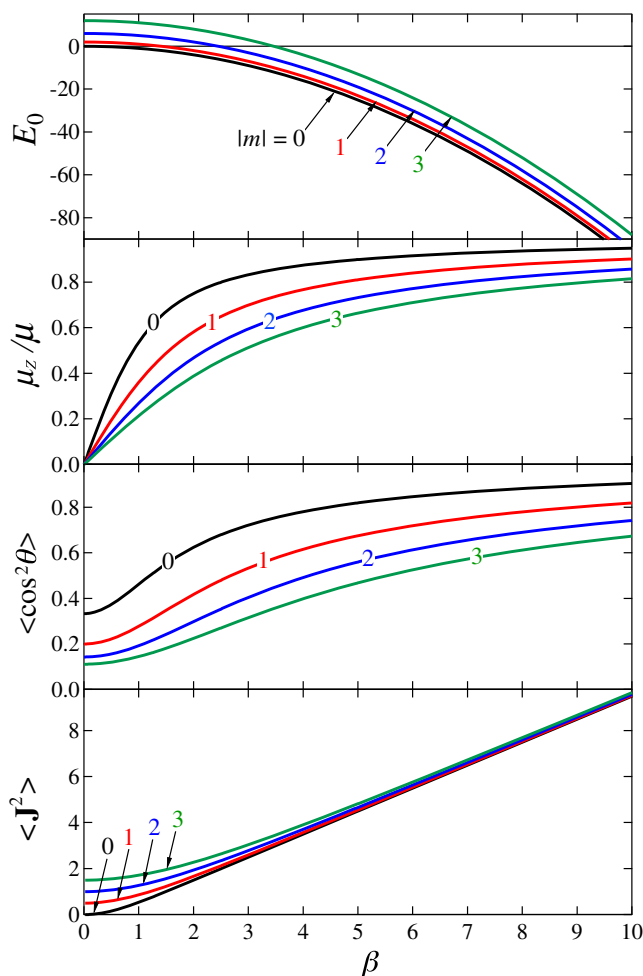


Figure 3. Ground-state energies E_0 (in units of the rotational constant B), space-fixed dipole moments $\mu_z/\mu \equiv \langle \cos \theta \rangle$, alignment cosines $\langle \cos^2 \theta \rangle$ and expectation values of the angular momentum $\langle \mathbf{J}^2 \rangle$ for different $|\tilde{J} = m, m; \beta\rangle$ states as a function of the interaction parameter β .

6. Applications

The analytic wavefunctions of molecules in combined fields make it possible to obtain their properties analytically as well. The space fixed dipole moment, μ_z , is given by the orientation cosine, $\langle \cos \theta \rangle = \langle \psi(\theta) | \cos \theta | \psi(\theta) \rangle$, and for the exact wavefunction of equation (31) can be evaluated in closed form,

$$\mu_z/\mu \equiv \langle \cos \theta \rangle = \frac{I_{m+3/2}(2\beta)}{I_{m+1/2}(2\beta)}, \quad (50)$$

where $I_n(z)$ is a modified Bessel function of the first kind [14]. Figure 3 shows spaced fixed dipole moments corresponding to the states $|\tilde{J} = m, m; \beta\rangle$ for several values of m as a function of the β parameter. The value of μ_z rapidly increases with β . For instance, for $m = 0$, it rises from only 0.54μ at $\beta = 1$ to 0.83μ at $\beta = 3$. In the case of the much studied $^{40}\text{K}^{87}\text{Rb}$ molecule, which possesses a dipole moment $\mu = 0.589$ Debye and a polarizability anisotropy

$\Delta\alpha = 54.21 \text{ \AA}^3$ [21, 22], relatively weak fields of $\varepsilon = 38 \text{ kV cm}^{-1}$ and $I = 1.75 \times 10^9 \text{ W cm}^{-2}$ (corresponding to $\beta = 5$) give rise to a strongly oriented ground state with $\mu_Z = 0.9\mu$. This value of $\langle \cos \theta \rangle$ corresponds to the molecular axis confined to librate within $\pm 26^\circ$ about the common direction of the fields.

The alignment cosine, $\langle \cos^2 \theta \rangle = \langle \psi(\theta) | \cos^2 \theta | \psi(\theta) \rangle$, characterizes the molecular alignment along the Z -axis. For the wavefunction of equation (31), the alignment cosine takes the analytic form

$$\langle \cos^2 \theta \rangle = \frac{2\beta^2 {}_0\tilde{F}_1(; m+7/2; \beta^2) + {}_0\tilde{F}_1(; m+5/2; \beta^2)}{2 {}_0\tilde{F}_1(; m+3/2; \beta^2)}, \quad (51)$$

with ${}_0\tilde{F}_1(; a; z) = {}_0F_1(; a; z) / \Gamma(a)$ being a regularized confluent hypergeometric function [14]. Figure 3 shows $\langle \cos^2 \theta \rangle$ of the states $|\tilde{J} = m, m; \beta\rangle$ for several values of m as a function of the β parameter. The $|0, 0; \beta\rangle$ state exhibits quite a strong alignment with the alignment cosine rapidly approaching with increasing β the value of 0.8, which corresponds to a libration of the molecular axis about the polarization vector of the radiative field with an angular amplitude of 27° .

The expectation value of the angular momentum is related to the orientation cosine, equation (50), via

$$\langle \mathbf{J}^2 \rangle = \frac{m}{2} + \beta \frac{I_{m+3/2}(2\beta)}{I_{m+1/2}(2\beta)} \equiv \frac{m}{2} + \beta \langle \cos \theta \rangle. \quad (52)$$

We note that the dependence of $\langle \mathbf{J}^2 \rangle$, shown in figure 3, becomes asymptotically linear in β for all the values $|m|$, cf equation (52).

By making use of equations (5) and (17), one can show that the following condition for the expectation values is satisfied:

$$\langle \mathbf{J}^2 \rangle + m^2 \left\langle \frac{1}{\sin^2 \theta} \right\rangle - 2\beta(m+1) \langle \cos \theta \rangle - \beta^2 \langle \cos^2 \theta \rangle \equiv E_0, \quad (53)$$

with the energy E_0 given by equation (16).

Table 1 lists, for reference purposes, the above analytic expressions for the space-fixed dipole moment, alignment cosine and expectation value of the angular momentum for different values of $|m|$.

7. Conclusions

By invoking SUSY, we found the condition under which the molecular Stark effect problem becomes exactly solvable. The condition, $\Delta\omega = \frac{\omega^2}{4(m+1)^2}$, cf equation (17), connects values of the parameters ω and $\Delta\omega$ that characterize the interaction strengths of a polar and polarizable molecule with collinear electrostatic and nonresonant radiative fields. The exact solutions are obtained for the $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ family of ‘stretched’ states.

We also considered the field-free and strong-field limits of the combined-field problem and found that both exhibit supersymmetry and shape invariance, which is indeed the reason why they are analytically solvable.

By making use of the analytic form of the $|\tilde{J} = m, m; \omega, \Delta\omega\rangle$ wavefunctions, we derived simple analytic formulae for the expectation values of the space-fixed electric dipole moment, the alignment cosine and the angular momentum. These key characteristics of molecules in

Table 1. Analytic expressions for the space-fixed dipole moment $\mu_z/\mu \equiv \langle \cos \theta \rangle$, alignment cosine $\langle \cos^2 \theta \rangle$ and expectation value of the angular momentum $\langle \mathbf{J}^2 \rangle$ obtained from equations (50)–(52) for different values of $|m|$.

$ m $	$\mu_z/\mu \equiv \langle \cos \theta \rangle$	$\langle \cos^2 \theta \rangle$	$\langle \mathbf{J}^2 \rangle$
0	$\coth(2\beta) - \frac{1}{2\beta}$	$1 + \frac{1}{2\beta^2} - \frac{\coth(2\beta)}{\beta}$	$\beta \coth(2\beta) - \frac{1}{2}$
1	$\frac{2\beta}{2\beta \coth(2\beta) - 1} - \frac{3}{2\beta}$	$5 + \frac{3}{\beta^2} + \frac{8\beta}{\tanh(2\beta) - 2\beta}$	$\frac{2\beta^2}{2\beta \coth(2\beta) - 1} - 1$
2	$\frac{8\beta^3}{3(4\beta^2 - 6\beta \coth(2\beta) + 3)}$ $-\frac{2\beta}{3} - \frac{5}{2\beta}$	$3 + \frac{15}{2\beta^2} - \frac{8\beta^2}{3 + 4\beta^2 - 6\beta \coth(2\beta)}$	$\frac{3}{2} - \frac{2\beta^2}{3}$ $+ \frac{8\beta^4}{3(3 + 4\beta^2 - 6\beta \coth(2\beta))}$
3	$\frac{\begin{bmatrix} (16\beta^4 + 180\beta^2 + 105) \\ -10\beta(8\beta^2 + 21) \coth(2\beta) \end{bmatrix}}{\begin{bmatrix} 4\beta^2(4\beta^2 + 15) \coth(2\beta) \\ -6\beta(8\beta^2 + 5) \end{bmatrix}}$	$\frac{\begin{bmatrix} 2\beta(4\beta^4 + 95\beta^2 + 210) \coth(2\beta) \\ -(56\beta^4 + 375\beta^2 + 210) \end{bmatrix}}{\begin{bmatrix} 2\beta^3(4\beta^2 + 15) \coth(2\beta) \\ -3\beta^2(8\beta^2 + 5) \end{bmatrix}}$	$\frac{\begin{bmatrix} -4\beta(7\beta^2 + 15) \coth(2\beta) \\ +2(4\beta^4 + 27\beta^2 + 15) \end{bmatrix}}{\begin{bmatrix} 2\beta(4\beta^2 + 15) \coth(2\beta) \\ -3(8\beta^2 + 5) \end{bmatrix}}$

fields are summarized in table 1. We also derived a ‘sum rule’ that yields a formula for the corresponding eigenenergy, equation (53), in terms of the above expectation values. The analytic expressions obtained open a direct route to engineering molecular states with preordained characteristics.

Interestingly, it is possible to glean the reason why the exact solution of equation (8) is obtained for only one particular relation between the field strength parameters, equation (17), from the semiclassical (WKB) approximation [23]. The eigenfunction of a 1D Schrödinger equation assumes the WKB form $f(\theta) \propto \exp[iS(\theta)]$, with $S(\theta)$ being the action of the underlying classical system. For the ground state of the potential (19), the action satisfies the differential equation, $S'(\theta)^2 - iS'(\theta) = V_-^{(1D)}$, whose solutions are obtained by expanding $S(\theta)$ in powers of \hbar . It turns out that in the case of the combined field strengths connected via equation (17), the series converges to the following exact expression:

$$S(\theta) = \frac{1}{2i} [2\beta \cos \theta + (2m + 1) \ln(\sin \theta)], \quad (54)$$

which, when substituted into $f(\theta)$, yields the exact, closed-form wavefunction, equation (27).

We note that the exact ground-state wavefunction $|\tilde{J} = 0, m = 0; \omega = 0, \Delta\omega\rangle$ can also be obtained as a ‘curious eigenproperty’ by the method outlined by von Neumann and Wigner in 1929. They showed that by imposing the integrability condition on the sought wavefunction, a class of potentials could be derived that support a localized bound state embedded in the continuum [24–26].

An extension of the method described in section 3 might furnish other types of exact wavefunctions for the case of more than two combined fields and for non-collinear field geometries.

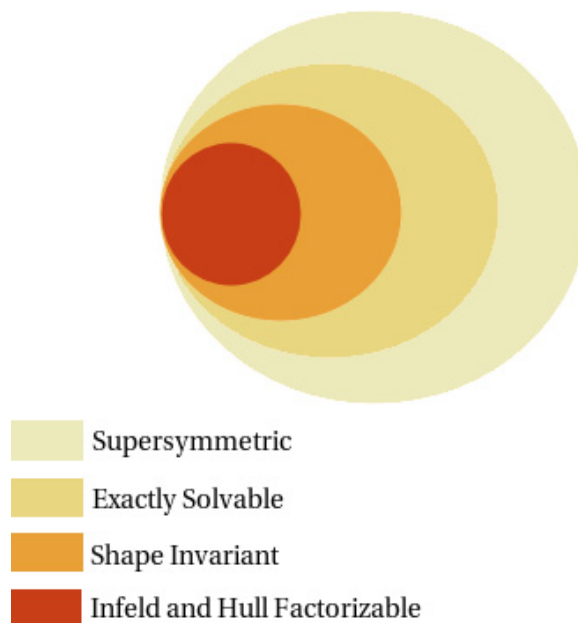


Figure A.1. A Venn diagram showing the relationships among supersymmetric, exactly solvable, shape invariant and Infeld and Hull factorizable potentials.

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Appendix. Exactly solvable, shape invariant and Infeld–Hull factorizable potentials

SUSY, shape invariance, exact solvability and the factorization method are often studied concurrently in the literature. In this appendix, we briefly survey the literature dealing with the relationships among them. Figure A.1 summarizes the results.

Every 1D potential with a ground state in closed form admits SUSY. Given a 1D quantum system with at least one bound state, one can find a partner Hamiltonian that has exactly the same discrete spectrum except for the ground-state energy of H_- [27, 28].

Every Infeld and Hull factorizable potential is shape invariant but the converse is not true. Shape invariance offers, in general, more than the factorization method, since the factorization method treats only the translational shape invariance [28, 29]. The table prepared by Infeld and Hull [12], although complete for most purposes, is not the most general table possible, as it does not include the most general solution of the Riccati equations, worked out in [29].

Shape invariance and normalizability are sufficient but not necessary conditions for exact solvability. Gendenshtein suggested that all exactly solvable potentials must be shape invariant [5], but many counterexamples to this conjecture were later constructed: for instance, the Natanzon class of potentials, which are, in general, not shape invariant [19, 30, 31]. We also note that in order to be exactly solvable, the shape-invariant potentials should admit normalizable solutions.

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